

TITLE: THE REMOVAL OF SULFUR DIOXIDE (SO₂) FROM FLUE GAS USING UTILITY SYNTHESIZED ZEOLITES DATE: April 1998

PI: Michael W. Grutzeck (gur@psu.edu)

STUDENT: Anand Srinivasan, Master of Engineering Candidate

INSTITUTION: The Pennsylvania State University
Materials Research Laboratory
University Park, PA 16802
(814) 863-2779

GRANT NO.: DE-FG22-96PC96210

PERIOD OF PERFORMANCE: September 1, 1996 to August 31, 1999

Title: THE REMOVAL OF SULFUR DIOXIDE (SO₂) FROM
FLUE GAS USING UTILITY SYNTHESIZED ZEOLITES

Authors Michael W. Grutzeck and Anand Srinivasan
gur@psu.edu
814-863-2779 (phone)
814-863-7040 (fax)
The Pennsylvania State University
Materials Research Laboratory
University Park, PA 16802

Abstract

The removal of sulfur dioxide (SO₂) from flue gases became mandated by NSPS more than 25 years ago. To comply, utilities have made a choice, either scrub using a lime-based scrubbing system or burn low-sulfur containing coal. The majority of the coal burning utilities in Pennsylvania have chosen lime-based scrubbing. Although lime based scrubbing is a proven technology it does have a number of serious drawbacks. In addition to the costs associated with purchasing lime-based scrubbing materials and the cost of disposing of the waste sulfate/sulfite that is generated, the use of lime based materials based on calcite (CaCO₃) always add additional CO₂ to the atmosphere. Once CO₂ becomes a monitored greenhouse gas, this could be a costly consequence of this technology. The work accomplished during the current year of funding explores a different way of dealing with SO₂ emissions, a method that could allow the remaining non-scrubbing utilities in Pennsylvania to once again burn sulfur-rich Pennsylvania coal.

The idea of using zeolites to clean-up off gas emissions is not new. Sulfuric acid manufacturing plants have been the most common industrial users of zeolites to clean-up their SO₂ emissions. More recently, Chriswell and Gollakota (1987), and Gollakota and Chriswell (1988) published papers that showed that the use of acid resistant Silicalite (a synthetic zeolite molecular sieve manufactured by Union Carbide Corporation) would give zero release and adsorb ~38 mg SO₂ per gram of zeolite at 25°C from a simulated coal burning flue gas. The technology works very well, but normally synthetic zeolites at \$800 a ton are too costly to compete with lime-based scrubbing.

The work accomplished during the first full year of the grant was to explore the possibility of a utility synthesizing its own zeolites from their own fly ash and then using the zeolites to remove SO₂. To date, the project has been successful. However, removal efficiencies are about 1/6th that of Silicalite (6 mg per g solid), but the fly ash samples are only partially converted and still contain a significant amount of unreacted fly ash. Work is continuing to increase reactivities using more alkaline solutions, ball milling of the fly ash, and zeolite seeds.

To date, zeolites have been synthesized from a total of 5 Class F fly ashes. Two were obtained from Allegheny Power and three were obtained from Pennsylvania Power & Light. The fly ashes ranged from the very clean concrete-grade fly ashes to the very carbon-rich fly ashes with high losses on ignition. The fly ashes were mixed with 1N and 3N sodium hydroxide and cured at 60°, 90° and 150°C as a function of

time. The most common zeolites that formed were Zeolite Na-P1, X and Y below 100°C and analcime and hydroxysodalite above 100°C. In addition to zeolites, the samples also typically contained residual mullite and glass from the fly ash.

A UV/VIZ spectrophotometer was used to monitor the amount of SO₂ in a simulated flue gas (O₂, N₂, CO₂ and 2000 ppm SO₂). The gas was passed through a 10 cc fixed bed adsorber containing the zeolite samples. The spectrophotometer was set on the resonance frequency of SO₂, therefore, when SO₂ was adsorbed by the zeolites, adsorption fell to zero. The rate of passage of the gas was 10cc/sec and the powdered sample size was typically 1 gram. The best adsorption was found to occur when samples were synthesized at 150°C and were microwave dried for 8 minutes prior to being tested. The nature of the fly ash played a minor role. All fly ashes, regardless of their carbon content, tended to produce the same zeolites when reacted under the same conditions.

Zeolites can be manufactured as rather robust granules which can be placed on a metal mesh conveyer belt which would, at some predetermined interval, refresh itself with a new load of zeolite granules. The intermittently movable bed of zeolite adsorber could be placed at the back end of the bag house where temperatures are lower and the chances of the bed clogging with fly ash less of a problem. Zeolites tend to provide zero release for the entire period that they are adsorbing SO₂. Breakthrough occurs rather rapidly and dramatically. Thus they are ideally suited for an intermittently refreshed filter bed operation. The fully charged material can be heated to extract the SO₂ and then reused, or sold as an acidifying soil conditioner for acid loving plants.

References

Chriswell, C. and S. Gollakota, "Adsorption of Sulfur Dioxide from Combustion Gases on a Regenerable Molecular Sieve", Preprints of Papers, Amer. Chem. Soc., Div. Fuel Sci. 32 (1) 505-12 (1987).

Gollakota, S.V. and C.D. Chriswell, "Study of an Adsorption Process Using Silicalite for Sulfur Dioxide Removal from Combustion Gases", Industrial Eng. Chem. Res. 27, 139-43 (1988).

List of Publications

Grutzeck, M.W. and D.D. Siemer, "Zeolites Synthesized from Class F Fly Ash and Sodium Aluminate Slurry," J. American Ceramic Society 80, 2449-53 (1997). Partial Support

Srinivasan, A. and M.W. Grutzeck, "The Adsorption of SO₂ by Zeolites Synthesized from Fly Ash," Submitted to J. Environmental Science and Technology (1998).

Srinivasan, A., "Adsorption of Sulfur Dioxide by Zeolites Synthesized from Fly Ash," M.E. Report, Submitted in Partial Fulfillment of the Requirements for the Degree of Master of Environmental Engineering (May 1998).

Grutzeck, M.W., "Using Zeolites Synthesized from Fly Ash to Remove SO₂, NO_x and NH₃ From Flue Gases," In preparation.

List of Presentations

Srinivasan, A. and M.W. Grutzeck, "The Adsorption of SO₂ by Zeolites Synthesized from Fly Ash," 1997 Materials Research Society Meeting, Boston (1997).